Pyradoketosite, a new, unexpected, polymorph of Ag$_3$SbS$_3$ from the Monte Arsiccio mine (Apuan Alps, Tuscany, Italy)

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ABSTRACT

Although everything seemed clear about the Ag-Sb-S compounds belonging to one of the more deeply studied experimental systems, nature allowed us to discover a new polymorph of Ag$_3$SbS$_3$, which could represent a compound for assessing new technological potentialities. The new mineral species pyradoketosite, Ag$_3$SbS$_3$ (IMA 2019-132), was discovered in the pyrite + baryte + iron oxide ore deposit of the Monte Arsiccio mine, Apuan Alps, Tuscany, Italy. It occurs as brittle orange acicular crystals, up to 200 μm in length and 25 μm in thickness, with adamantine luster. Under reflected light, pyradoketosite is slightly bluish-gray, with abundant orange internal reflections. Bireflectance is weak, and anisotropism was not observed, being masked by abundant internal reflections. Minimum and maximum reflectance data for the wavelengths recommended by the Commission on Ore Mineralogy [R$_{\min}$/R$_{\max}$ (%)] (λ, μm) are 32.8/32.9 (470), 30.2/30.7 (546), 29.0/29.6 (589), and 27.5/28.4 (650). Electron microprobe analysis gave (mean of 6 spot analyses, in wt%): Ag 59.81, Sb 22.63, S 17.78, total 100.22. On the basis of (Ag+Sb) = 4 atoms per formula unit, the empirical formula of pyradoketosite is Ag$_{6.9350(6)}$Sb$_{1.004(11)}$S$_{3.696(15)}$. Pyradoketosite is monoclinic, space group $P2_1/n$, with $a = 13.7510(15)$, $b = 6.9350(6)$, $c = 19.555(2)$ Å, $β = 94.807(4)^\circ$, $V = 1858.3(3)$ Å$^3$, $Z = 12$. The crystal structure was solved and refined to $R_1 = 0.063$ on the basis of 2682 unique reflections with $F_o > 4σ(F_o)$ and 191 refined parameters. The structure of pyradoketosite can be described as formed by the alternation of {101} layers: an Sb-rich layer, Sb$_4$AgS$_6$, and two distinct Ag$_6$S$_4$ layers. This layered organization allows identifying structural relationships with the wittichenite-skinnerite pair. Pyradoketosite is associated with pyrargyrite, tetrahedrite-(Hg), valentinite, and probable pyrostilpnite in baryte + dolomite + quartz veins embedded in metadolostone. Its name derives from the old Greek words “πυρ” (fire) and “αὐδοχηστος” (unforeseen), because of the unexpected occurrence of this third polymorph of the compound Ag$_3$SbS$_3$.

Keywords: Pyradoketosite, silver, antimony, sulfosalt, crystal structure, new mineral, Monte Arsiccio mine, Apuan Alps, Tuscany, Italy

INTRODUCTION

More than 150 Ag-chalcogenides are currently known as valid mineral species, mainly represented by sulfosalts (e.g., Moëlo et al. 2008; Bindi and Biagioni 2018). Indeed, silver is a chemical constituent of several minerals belonging to important groups of sulfosalts, e.g., sartorite (Makovicky and Topa 2015), lillianite (e.g., Makovicky and Topa 2014), polybasite (e.g., Bindi et al. 2007, 2020), and tetrahedrite (Biagioni et al. 2020b) groups. Despite the wide number of mineral species, the Ag–Sb–S system currently has only six approved sulfosalts, i.e., baumstarkite, cuboargyrite, miargyrite, pyrargyrite, pyrostilpnite, and stephanite. Baumstarkite (triclinic), cuboargyrite (cubic), and miargyrite (monoclinic) can be considered polymorphs of the compound AgSbS$_3$ (Smith et al. 1997; Walenta 1998; Effenberger et al. 2002), although Kitakaze et al. (2012) questioned the dimorphic relations between baumstarkite and miargyrite. Trigonal pyrargyrite and monoclinic pyrostilpnite are the two known dimorphs of Ag$_3$Sb$_5$S$_8$ (Laufek et al. 2010; Biagioni et al. 2020c), with the latter being the low-$T$ polymorph (e.g., Chang 1963; Keighin and Honea 1969). Stephanite, Ag$_3$Sb$_5$S$_8$, is another low-$T$ Ag-sulfosalts, stable below 197 ± 5 °C (e.g., Keighin and Honea 1969), with orthorhombic symmetry (Leitl et al. 2009).

During the study of the sulfosalts assemblages of the Monte Arsiccio mine (Apuan Alps, northern Tuscany, Italy), two samples showing micrometer-sized acicular crystals, orange in color, were observed. Electron microprobe and single-crystal X-ray diffraction studies showed it to be a new polymorph of Ag$_3$SbS$_3$. The mineral and its name were approved by the Commission on New Minerals, Nomenclature and Classification of...